



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Comparison of independent D14CO2 records at Point Barrow, Alaska

H. D. Graven, X. Xu, T. P. Guilderson, R. F.  
Keeling, S. E. Trumbore, S. Tyler

April 9, 2013

Radiocarbon

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

# Comparison of independent $\Delta^{14}\text{CO}_2$ records at Point Barrow, Alaska

H. D. Graven<sup>1,\*</sup>, X. Xu<sup>2</sup>, T. P. Guilderson<sup>3,4</sup>, R. F. Keeling<sup>1</sup>, S. E. Trumbore<sup>5</sup>, S. Tyler<sup>2</sup>

1. Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0244, USA

2. Department of Earth System Science, University of California, Irvine, Irvine, CA 92697-3100, USA

3. Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory L-397, 7000 East Ave., Livermore, CA 94550, USA

4. Department of Ocean Sciences, University of California, Santa Cruz, Santa Cruz, CA 95064, USA

5. Max Planck Institute of Biogeochemistry, Postfach 10 01 64, 07701 Jena, Germany

\*Correspondence to: hgraven@ucsd.edu

Two independent programs have collected and analyzed atmospheric  $\text{CO}_2$  samples from Point Barrow, Alaska for radiocarbon content ( $\Delta^{14}\text{C}$ ) over the period 2003-2007. In one program, flask collection, stable isotope analysis and  $\text{CO}_2$  extraction are performed by the Scripps Institution of Oceanography's  $\text{CO}_2$  Program and  $\text{CO}_2$  is graphitized and measured by accelerator mass spectrometry at Lawrence Livermore National Laboratory. In the other program, the University of California, Irvine performs flask collection, sample preparation and accelerator mass spectrometry. Over 22 common sample dates spanning five years, differences in measured  $\Delta^{14}\text{C}$  are consistent with the reported uncertainties and there is no significant bias between the programs.

## 1. Introduction

A standard method to assess the comparability of radiocarbon laboratories is to distribute common materials for independent processing and analysis at each laboratory (Polach 1989; Scott 2003), including  $\text{CO}_2$  in dry air (Miller et al. 2011, 2012). For laboratories analyzing radiocarbon content ( $\Delta^{14}\text{C}$ ) in atmospheric  $\text{CO}_2$ , a more complete intercomparison is possible using duplicate atmospheric samples collected at the same location and time. This allows for comparing all factors influencing the measurements, including sampling, storage, processing, and analysis. Such co-located sampling programs have been utilized for assessing comparability of laboratories measuring the concentration of atmospheric  $\text{CO}_2$  and other atmospheric compounds (Hudec and Trivett 1997; Masarie et al. 2001), but they have not yet been employed for  $\Delta^{14}\text{C}$  in  $\text{CO}_2$  measured by accelerator mass spectrometry (AMS).

Here we compare two independent measurement programs for  $\Delta^{14}\text{C}$  in  $\text{CO}_2$  at Point Barrow, Alaska. One program is run by a collaboration between the Scripps Institution of Oceanography and Lawrence Livermore National Laboratory (SIO/LLNL), and the other program is run by the University of California, Irvine (UCI). The programs employ whole air flask sampling,  $\text{CO}_2$

extraction and graphitization, and accelerator mass spectrometry using slightly different techniques described in Section 2.

Our analysis focuses on a statistical comparison of  $\Delta^{14}\text{C}$  measurements on groups of samples that were collected on the same date by both programs. We determine whether the differences in  $\Delta^{14}\text{C}$  are commensurate with the reported measurement uncertainties and evaluate the data for any consistent bias in  $\Delta^{14}\text{C}$  between the two programs.

## **2. Methods**

### **2.1 SIO/LLNL measurements**

The Scripps  $\text{CO}_2$  Program collects whole air samples at Point Barrow using 5 liter glass flasks that have been pre-evacuated at SIO (Keeling et al. 2002). Flasks are filled to atmospheric pressure by opening a single glass stopcock sealed with Apiezon<sup>®</sup> grease.  $\text{CO}_2$  concentration is measured in the flask at SIO and then  $\text{CO}_2$  is extracted cryogenically from a portion of the remaining air and sealed in Pyrex tubes. Each sample is approximately 0.5 mg C in size.

At LLNL,  $\text{CO}_2$  samples are converted to graphite by reducing with  $\text{H}_2$  gas over an iron catalyst and then measured by AMS (Graven et al. 2007, Graven 2008). Measurements are reported as  $\Delta^{14}\text{C}$  [equivalent to  $\Delta$  in the work by Stuiver and Polach [1977]], where  $\delta^{13}\text{C}$  measurements from concurrent samples (Keeling et al. 2001) are used to correct for mass dependent fractionation. Total measurement uncertainty for  $\Delta^{14}\text{C}$  in  $\text{CO}_2$  is  $\pm 1.7\text{--}2.8\text{‰}$  (Graven et al. 2007; Graven 2008; Graven et al. 2012).

### **2.2 UCI measurements**

The UCI program collects whole air samples at Point Barrow using 6 liter one-valve stainless steel canisters (Silco Can, Restek Co) that have been pre-evacuated at UCI (Xu et al. 2007a). The canisters are pressurized to approx. 2 atm using an oil-free pump (Tyler et al. 2007). For the period from 6/17/05-3/17/06, six air samples that are included in this study were collected using 32 L one-valve stainless steel canisters (Tyler et al., 2007). Subsamples were then taken from these samples for  $^{14}\text{C}$  analysis.  $\text{CO}_2$  is extracted cryogenically at UCI then converted to graphite by the sealed tube zinc reduction method (Xu et al. 2007b). Each sample is approximately 2.7 mg C in size. Analysis of  $\Delta^{14}\text{C}$  is performed at the W.M. Keck AMS facility at UCI with total measurement uncertainty of  $\pm 1.3\text{--}2.4\text{‰}$  (Xu et al. unpublished data). Mass dependent fractionation is corrected for using “on-line”  $\delta^{13}\text{C}$  measurements during AMS analysis, which accounts for fractionation that occurred during graphitization and inside the AMS.

### **2.3 Comparison of the two programs**

The observations from SIO/LLNL and UCI overlap for the period 2003-2007, with 22 individual sample dates common to both programs (Figure 1). For 13 of the 22 sample dates, replicate samples were collected and analyzed for  $\Delta^{14}\text{C}$  by the UCI program. No replicate observations were made by the SIO/LLNL program.

We compare the observations by first averaging any replicate measurements from UCI, then averaging the mean  $\Delta^{14}\text{C}$  from UCI with the  $\Delta^{14}\text{C}$  measured by SIO/LLNL. We calculate the residual by subtracting this overall mean from the  $\Delta^{14}\text{C}$  measured by each program. The bias is given by the difference in the average residual for UCI and SIO/LLNL ( $\mu_{\text{UCI}}$  and  $\mu_{\text{SIO/LLNL}}$ ), which is compared to the standard error to assess significance.

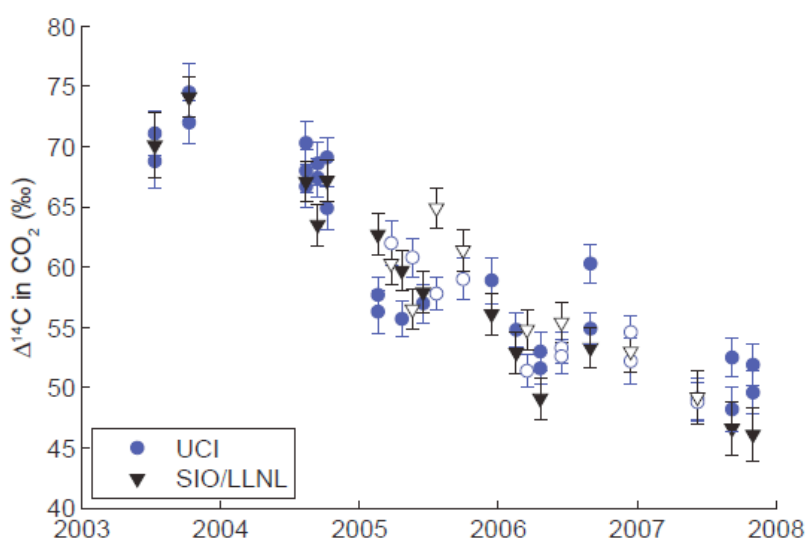


Figure 1. Observations of  $\Delta^{14}\text{CO}_2$  at Point Barrow, Alaska for sample dates in common from the SIO/LLNL and UCI measurement programs. Filled symbols indicate the UCI and SIO flasks were collected within an hour of each other, empty symbols indicate the SIO flask was collected 4-6 hours later than the UCI flask on that date.

Flasks from both programs are filled by NOAA personnel at the Point Barrow station, who check for clean air conditions prior to filling flasks for trace gas and isotope analyses. Most of the SIO and UCI flasks were collected within an hour of each other on each sample date, with sampling times between 8:00 and 15:30 local time. However, for 8 sample dates, indicated by empty symbols in Figure 1, the SIO flask was collected 4-6 hours later than the UCI flask(s). We also perform separate calculations of the bias for samples collected with larger time differences, in case the measurements are affected by natural daily variations.

### 3. Results

There is very good agreement between the  $\Delta^{14}\text{CO}_2$  measurements from the SIO/LLNL and UCI programs at Point Barrow. The residual  $\Delta^{14}\text{C}$  is within  $\pm 1\sigma$  for 60% of the sample dates, and within  $\pm 2\sigma$  for all but one sample date (Figure 2). For 5 of the 13 sample dates with replicate samples from UCI, the SIO/LLNL measurement was bracketed by the UCI measurements (Figure 1). Correspondence between the two laboratories is consistent with their average reported uncertainties of  $\pm 1.7\text{‰}$ .

There is no significant bias between the two programs. The difference in the average residuals is  $0.2 \pm 0.7\text{‰}$  for UCI compared to SIO/LLNL (Figure 2, Table 1). Including only the samples collected with an hour of each other increases the mean bias to  $1.0\text{‰}$ , but it remains similar to the standard error of  $\pm 0.9\text{‰}$ . Likewise, the mean bias in the samples collected more than four hours apart is not significantly different from zero ( $-1.2 \pm 1.3\text{‰}$ , Table 1).

Diurnal variations of  $\Delta^{14}\text{C}$  have not been characterized at Point Barrow, but observations of  $\text{CO}_2$  concentration vary by only  $\pm 0.4\text{ ppm}$  between the morning and afternoon (Thoning et al. 2012). Making the extreme assumption that this variation was due to radiocarbon-free  $\text{CO}_2$ , this would cause  $\Delta^{14}\text{C}$  to vary by only  $\pm 1\text{‰}$ , which we can take as an upper bound to the corresponding  $\Delta^{14}\text{C}$  variability. Our observations also indicate that diurnal cycles in  $\Delta^{14}\text{C}$  at Point Barrow are small, and that samples collected at different times of day are likely to have consistent  $\Delta^{14}\text{C}$  values. A lack of diurnal variation reflects the remoteness of Point Barrow, differing from sampling stations located near to local fossil fuel emission sources where  $\Delta^{14}\text{C}$  is typically higher in the afternoon because of enhanced ventilation of emissions (Graven et al. 2009; Newman et al. 2012).

Table 1. Bias (UCI-SIO/LLNL) and standard error in all samples, in samples collected within one hour of each other and in samples collected more than four hours apart.

Group	Bias and standard error
All samples	$0.2 \pm 0.7\text{‰}$
Collected within one hour	$1.0 \pm 0.9\text{‰}$
Collected more than 4 hours apart	$-1.2 \pm 1.3\text{‰}$

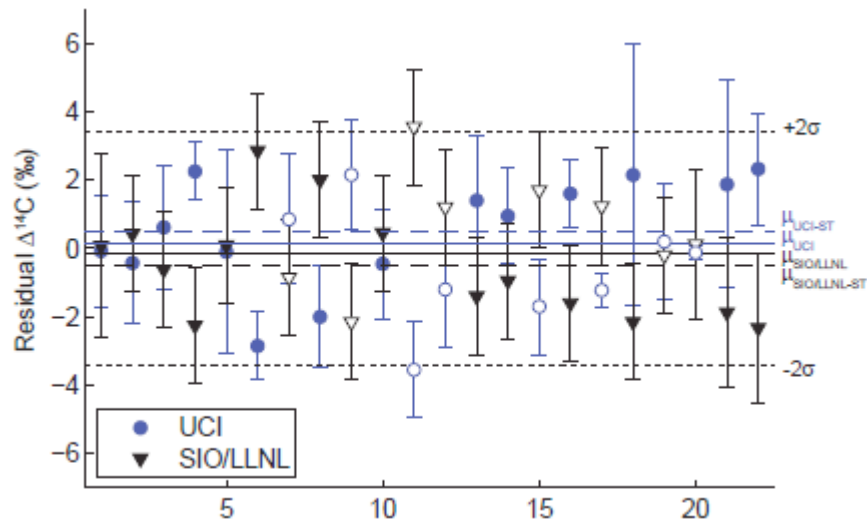


Figure 2. Residual  $\Delta^{14}\text{C}$  for 22 individual sample dates. Replicate samples from UCI have been averaged. Error bars show the reported measurement uncertainty or, for UCI, the standard deviation in replicate measurements. The average residuals,  $\mu_{\text{UCI}}$  and  $\mu_{\text{SIO/LLNL}}$ , are shown by solid lines. The average residuals for samples collected within one hour of each other only,  $\mu_{\text{UCI-ST}}$  and  $\mu_{\text{SIO/LLNL-ST}}$ , are shown by dashed lines. Dotted lines show a  $\pm 2\sigma$  envelope around the average reported uncertainty of  $\pm 1.7$  ‰.

#### 4. Conclusions

Our comparison shows there is no significant bias between measurements of  $\Delta^{14}\text{C}$  in atmospheric  $\text{CO}_2$  conducted by SIO/LLNL and UCI at Point Barrow. The two programs meet the  $\pm 1$  ‰ criteria for comparability recommended by the WMO (2011). As SIO/LLNL and UCI both perform  $\Delta^{14}\text{C}$  measurements at several other sites, this result suggests that observations from the two programs at other sites can be compiled and compared without adjustment of the reported data.

#### 5. Acknowledgments

We are grateful to NOAA and the Point Barrow field station personnel for collecting flask samples. Alane Bollenbacher performed stable isotopic analyses at SIO. A portion of this work was performed under the auspices of the U.S. Department of Energy under contract DE-AC52-07NA27344.

#### 6. References

149 Graven HD, Guilderson TP, Keeling RF. 2007. Methods for high-precision  $^{14}\text{C}$  AMS measurement  
150 of atmospheric  $\text{CO}_2$  at LLNL. *Radiocarbon* 49(2):349-356.

151 Graven HD. 2008. Advancing the use of radiocarbon in studies of global and regional carbon  
152 cycling with high precision measurements of  $^{14}\text{C}$  in  $\text{CO}_2$  from the Scripps  $\text{CO}_2$  Program. Ph.D.  
153 thesis. Scripps Inst. of Oceanogr., Univ. of Calif., San Diego, La Jolla.

154 Graven HD, Stephens BB, Guilderson TP, Keeling RF, Campos TL, Campbell JE, Schimel DS. 2009.  
155 Estimates of biospheric and fossil fuel-derived  $\text{CO}_2$  and fossil fuel  $\text{CO}_2$ :CO ratios from airborne  
156 measurements of  $\Delta^{14}\text{C}$ ,  $\text{CO}_2$ , and CO above Colorado. *Tellus B* 61(3):536-46.

157 Graven HD, Guilderson TP, Keeling RF. 2012. Observations of radiocarbon in  $\text{CO}_2$  at seven global  
158 sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles *J.*  
159 *Geophys. Res.* 117:D02303. doi:10.1029/2011JD016535.

160 Hudec VC, Trivett NBA. 1997. An evaluation of  $\text{CO}_2$  flask measurement programs at Alert,  
161 N.W.T., in *Report of the Eighth WMO Meeting of Experts on Carbon Dioxide Concentration*  
162 *and Isotopic Measurement Techniques, Boulder, USA, 6-11 July 1995*, WMO TD No. 821, pp.  
163 42-57, World Meteorol. Org. Global Atmos. Watch, Geneva.

164 Keeling CD, Piper SC, Bacastow RB, Wahlen M, Whorf TP, Heimann M, Meijer HA. 2001.  
165 Exchanges of atmospheric  $\text{CO}_2$  and  $^{13}\text{CO}_2$  with the terrestrial biosphere and oceans from 1978  
166 to 2000. I. Global aspects, SIO Reference Series, No. 01-06, Scripps Institution of  
167 Oceanography, San Diego, 88 pages.

168 Masarie KA et al. 2001. NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for  
169 directly assessing consistency among atmospheric measurements made by independent  
170 laboratories. *J. Geophys. Res.* 106(D17):20,445–20,464. doi:10.1029/2000JD000023.

171 Miller J, Wolak C, Lehman S, Allison C, Graven H, Guilderson T, Keeling R, Meijer H, Nakamura T,  
172 Nakazawa T, Neubert R, Smith A, Southon J, Xu X. 2011. Preliminary results from the first  
173 inter-comparison of Accelerator Mass Spectrometry atmospheric  $^{14}\text{CO}_2$  measurements, in  
174 *Report of the 15<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases*  
175 *and Related Tracers Measurement Techniques, 2009*, edited by W. Brand, Rep. 194, pp. 216-  
176 218, World Meteorol. Org. Global Atmos. Watch, Geneva.

177 Miller J, Wolak C, Lehman S, Allison C, Graven H, Guilderson T, Keeling R, LaFranchi B, Meijer H,  
178 Mukai H, Nakamura T, Nakazawa T, Neubert R, Smith A, Southon J, Terao Y, Xu X. 2012.  
179 Results of Three Rounds of an Inter-comparison of AMS-based Atmospheric  $^{14}\text{CO}_2$   
180 Measurements. Submitted to *Radiocarbon*.

181 Newman S, Jeong S, Fischer ML, Xu X, Haman CL, Lefer B, Alvarez S, Rappenglueck B, Kort  
182 EA, Andrews A, Peischl J, Gurney KR, Miller CE, and Yung YL. 2012. Diurnal tracking of  
183 anthropogenic  $\text{CO}_2$  emissions in the Los Angeles basin megacity during spring 2010. *Atmos.*  
184 *Chem. Phys. Discuss.* 12: 5771-5801. doi:10.5194/acpd-12-5771-2012.

185 Polach H. 1989.  $^{14}\text{C}$ CARE. *Radiocarbon* 31(3):422.



- 186 Scott EM. 2003. The Third International Radiocarbon Intercomparison (TIRI) and the Fourth  
187 International Radiocarbon Intercomparison (FIRI), 1990–2002. Results, Analyses, and  
188 Conclusions. *Radiocarbon* 45(2):135–408.
- 189 Thoning KW, Kitzis DR, Crotwell A. 2012. Atmospheric Carbon Dioxide Dry Air Mole Fractions  
190 from quasi-continuous measurements at Barrow, Alaska; Mauna Loa, Hawaii; American  
191 Samoa; and South Pole, 1973-2011. Version: 2012-05-07. Path:  
192 <ftp://ftp.cmdl.noaa.gov/ccg/co2/in-situ/>.
- 193 Tyler SC, Rice A, Ajie HL. 2007. Stable isotope ratios in atmospheric CH<sub>4</sub>: Implications for  
194 seasonal sources and sinks. *J. Geophys. Res.* 112:D03303. doi:10.1029/2006JD007231.
- 195 WMO. 2011. Expert Group Recommendations, in *Report of the 15<sup>th</sup> WMO/IAEA Meeting of CO<sub>2</sub>*  
196 *Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurements*  
197 *Techniques, Jena, Germany, 7-10 September 2009*, WMO TD No. 1553, pp. 1-37, World  
198 Meteorol. Org. Global Atmos. Watch, Geneva.
- 199 Xu X, Trumbore SE, Ajie H, Tyler S. 2007a.  $\Delta^{14}\text{C}$  of Atmospheric CO<sub>2</sub> over the Subtropical and  
200 Equatorial Pacific from Fall 2002 to Summer 2005 and at Point Barrow, Alaska, USA from 2002  
201 to 2007. *Eos Trans. AGU*, 88(52), Fall Meet. Suppl., Abstract B43D-1581.
- 202 Xu X, Trumbore SE, Zheng S, Southon JR, McDuffee KE, Luttgen M, Liu JC. 2007b. Modifying a  
203 sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing  
204 background and attaining high precision. *Nuclear Instruments and Methods in Physics*  
205 *Research B* 259:320–329.